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(54) Title: POLYOL COMPOSITION AND POLYISOCYANATE-BASED FOAM PREPARED THEREFROM

(57) Abstract: A polyol composition is disclosed that comprises an aromatic polyether polyol, preferably based on the condensation product of a phenol with an aldehyde and as blowing agent, formic acid. The polyol composition finds utility in the manufacture of polyurethane and particularly polyisocyanurate foams having attractive flameretardant and reduced smoke generation characteristics.

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POLYOL COMPOSITION AND  
POLYISOCYANATE-BASED FOAM PREPARED THEREFROM

5 The present invention relates to a process for preparing polyisocyanurate foam, and also to a polyol composition, having utility in the preparation of polyisocyanate-based foam.

10 Polyurethane and polyisocyanurate foam is being subjected to continuously changing and ever greater demands with respect to flame retardant and reduced smoke generation traits. It is also required that such foams are manufactured by processes that minimizes the use of blowing agents viewed as being harmful to the environment. Legislation has restricted the use of many substances traditionally used as physical blowing agent when preparing foam, and over the recent years there has been an emergence of alternative physical blowing agents including hydrocarbons, notably pentanes, and hydrofluoroalkanes such as for example tetrafluoroethane (R-134a) and pentafluoropropane  
15 (R-245fa).

There have also been many developments in the use of chemical blowing agents such as water and carbamates. Water is an attractive agent from the point of view of availability and economics. However, one of its disadvantages is the high consumption of isocyanate and high process temperatures associated with its use. Also in the case of polyisocyanurate foam, excessive amounts of water can be detrimental to foam properties leading to for example, high foam friability. An alternative to water is formic acid, which does not bring with it the same disadvantages. Formic acid reacts with isocyanate generating carbon monoxide and carbon dioxide gases that function as the blowing means.  
25

The literature contains a number of publications that disclose the use of formic acid as blowing agent when preparing polyisocyanate-based foams such as polyurethane or polyisocyanurate foams.

30 US Patent 4,417,002 discloses the use of formic acid in combination with water as blowing agent for the manufacture of polyurethane foams.

US Patent 5,143,945 discloses the preparation of rigid polyurethane-polyisocyanurate foams in the presence of a blowing agent comprising a halocarbon in combination with an organic carboxylic acid, and optionally water. The carboxylic acid can be formic acid.

5

US Patent 5,286,758 discloses the use of formic acid and formate salts to prepare a low density rigid polyurethane under conditions of improved reactivity control.

US Patent 5,214,076 teaches the preparation of a carbodiimide-isocyanurate open  
10 celled foam from aromatic polyester polyols or aromatic amine polyols (ethoxylated TDA) in the presence of a blowing agent that can comprise formic acid.

US Patents 5,478,494 and 5,770,635 teach a polyol composition comprising a mixture of polyether polyols of differing equivalent weights and use of such composition in  
15 the presence of formic acid to prepare rigid polyurethane foams.

US Patent 5,762,822 teaches the manufacture of rigid polyurethane foam from a froth foaming mixture that employs as blowing agent a C1-C4 hydrofluorocarbon having a boiling point of 300K or less in combination with at least 2 weight percent of formic acid or  
20 salts thereof. Similar teachings are also presented in US Patent 5,883,146.

Despite this apparently extensive knowledge relating to formic acid as blowing agent when manufacturing polyurethane or polyisocyanurate foam there is still a need to provide a foam that exhibits improved flame retardant performance or exhibits a reduced  
25 potential for smoke generation when burnt. Additionally for polyisocyanurate foam, the challenge is to combine above mentioned foam combustibility characteristics with convenient processing and generally acceptable foam mechanical properties .

It has now been discovered that formic acid-blown polyisocyanate-based foam  
30 prepared in the presence of an aromatic polyether polyol enables the production of foam with unexpected improvements in general physical performance including flame retardancy and smoke reduction.

In one aspect, this invention is a polyol composition suitable for the preparation of a rigid polyisocyanate-based foam, containing one or more polyether or polyester polyols and a blowing agent, wherein; (a) the blowing agent comprises formic acid; and (b) the polyol comprises an aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of a phenol with an aldehyde.

In a second aspect, this invention is a multi component system suitable for the preparation of a rigid polyisocyanate-based foam which comprises as first component an aromatic polyisocyanate, and as second component the polyol composition as mentioned above.

In a third aspect, this invention is a process for preparing a polyisocyanate-based foam which comprises bringing together under foam-forming conditions a polyisocyanate with the polyol composition as described above.

In a fourth and fifth aspect, this invention is a polyurethane foam, or a polyisocyanurate foam, obtained by bringing together under foam-forming conditions a polyisocyanate with a polyol composition characterized in that:

- a) the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 80 to 150 (for polyurethane) or from 150 to 600 (for polyisocyanurate); and
- b) the polyol composition comprises (i) formic acid; and (ii) an aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of a phenol with an aldehyde.

In a sixth aspect, this invention is a process for preparing a closed-celled polyisocyanurate foam by bringing into contact under foam-forming conditions a polyisocyanate with a polyol composition in the presence of a blowing agent mixture wherein the polyol composition comprises an aromatic polyester polyol and an aromatic polyether polyol; and wherein the blowing agent mixture comprises formic acid and an additional blowing agent, which is a hydrofluoroalkane selected from the group consisting of tetrafluoroethane, pentafluoropropane, heptafluoropropane and pentafluorobutane, or a hydrocarbon selected from the group consisting of butane, pentane, cyclopentane, hexane, cyclohexane, and heptane, and the isomers thereof, and wherein the polyisocyanate is

present in an amount to provide for an isocyanate reaction index of from greater than 150 to 600.

In a seventh aspect, this invention is a laminate comprising the above-mentioned polyurethane or polyisocyanurate foam.

5 The rigid polyisocyanate-based foams in accordance with this invention are prepared by bringing together under foam-forming conditions a polyisocyanate with a particular polyol composition comprising an aromatic polyol and a blowing agent comprising formic acid. The aromatic polyol is an aromatic polyether polyol or a combination thereof with an aromatic polyester polyol. The preferred aromatic polyether polyols are the aromatic  
10 polyoxyalkylene polyols based on an initiator derived from the condensation of a phenol with an aldehyde. In a preferred embodiment of this invention, the aromatic polyoxyalkylene polyol used is one obtained by reacting a condensate adduct of phenol and formaldehyde, with one or more alkylene oxides including ethylene oxide, propylene oxide, and butylene oxide. Such polyols, sometimes referred to as "Novolak" initiated polyols are  
15 known to one of skill in the art, and can be obtained by methods such as disclosed in, for example, US Patents Nos. 2,838,473; 2,938,884; 3,470,118; 3,686,101 and 4,046,721. Typically, "Novolak" starting materials are prepared by reacting a phenol (for example a cresol) with from 0.8 to 1.5 moles of formaldehyde per mole of the phenol in the presence of an acidic catalyst to form a polynuclear condensation product containing from 2.1 to 12,  
20 preferably from 2.2 to 6, and more preferably from 3 to 5 phenol units/molecule. The novolak resin is then reacted with an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide, or isobutylene oxide, to form an oxyalkylated product containing a plurality of hydroxyl groups. For the purpose of the present invention, preferred "Novolak" polyols are those having an average of from 3 to 6 hydroxyl moieties per molecule and an  
25 average hydroxyl equivalent weight of from 100 to 500, preferably from 100 to 300. The "Novolak" initiated polyether polyol preferably constitutes from about 1, more preferably from about 10, more preferably from about 20, and yet more preferably from about 25; and up to about 99, preferably to about 70, more preferably up to about 60 parts by weight of the total weight of polyol composition.

30 The polyol composition comprises the formic acid in an amount to provide foam of the desired density. Typically the formic acid is present in an amount of from 0.5 to 8 parts

per 100 parts by weight of the polyol composition including the formic acid. Preferably the formic acid is present an amount of from 1.5 parts and more preferably from 2 parts, and up to a preferred amount of 6 parts and more preferred 3.5 parts by weight.. While formic acid is the carboxylic acid of preference, it is also contemplated that minor amounts of other aliphatic mono and polycarboxylic acids may also be employed, such as those disclosed in US Patent 5,143,945 column 3, lines – column 4, line 28, and including isobutyric acid, ethylbutyric acid, and ethylhexanoic acid.

In addition to the “Novolak” polyol and formic acid, the polyol composition may contain other polyether and polyester polyols along with additional blowing agents, (for example water), catalysts, surfactants, fillers and Flame Retardant additives as commonly used in the manufacture of polyisocyanate-based foams.

Examples of additional blowing agents which can be present include hydrochlorofluorocarbons, hydrofluorocarbons and hydrocarbons, as well as water. The additional blowing agent is preferably used in an amount of from 2 to 15 parts preferably from 4 to 10 parts, per 100 parts by weight of the polyol composition. Suitable hydrofluoroalkanes are the C<sub>1</sub>-C<sub>4</sub> compounds including difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), 1,1-difluoroethane (R-152a), difluorochloroethane (R-142b), trifluoromethane (R-23), heptafluoropropane (R-227a), hexafluoropropane (R136), 1,1,1-trifluoroethane (R-133), fluoroethane (R-161), 1,1,1,2,2-pentafluoropropane (R-245fa), pentafluoropropylene (R2125a), 1,1,1,3-tetrafluoropropane, tetrafluoropropylene (R-2134a), 1,1,2,3,3-pentafluoropropane and 1,1,1,3,3-pentafluoro-n-butane. When a hydrofluorocarbon blowing agent is present, preferred is tetrafluoroethane (R-134a), pentafluoropropane (R-245fa) or pentafluorobutane (R-365). Suitable hydrocarbons for use as blowing agent include nonhalogenated hydrocarbons such as butane, isobutane, 2,3-dimethylbutane, n- and I-pentane isomers, hexane isomers, heptane isomers and cycloalkanes including cyclopentane, cyclohexane and cycloheptane. Preferred hydrocarbons for use as blowing agent include cyclopentane and notably n-pentane an isopentane. In a preferred embodiment of this invention the polyol composition comprises a physical blowing agent selected from the group consisting of tetrafluoroethane (R-134a), pentafluoropropane (R-245fa), pentafluorobutane (R-365), cyclopentane, n-pentane and isopentane. Water may also be present in the polyol composition added intentionally as a

blowing agent. When intending to prepare polyurethane foam advantageously water is present in an amount of from 0.5 to 10 parts, and preferably from 1 to 6 parts, per 100 parts by weight of the polyol composition. When intending to prepare a polyisocyanurate foam, in order to obtain facilitate and give desirable processing characteristics, it is advantageous  
5 not to exceed 2 parts of water, preferably not to exceed 1.5 parts of water, and more preferably not to exceed 0.75 parts of water; and even to have water absent.

Other polyols which may be present in the polyol composition include one or more other polyether or polyesters polyols of the kind typically employed in processes to make  
10 polyurethane foam. Other compounds having at least two isocyanate reactive hydrogen atoms may also be present, for example polythioether polyols, polyester amides and polyacetals containing hydroxyl groups, aliphatic polycarbonates containing hydroxyl groups, amine terminated polyoxyalkylene polyethers, and preferably, polyester polyols, polyoxyalkylene polyether polyols, and graft dispersion polyols. Mixtures of two or more of  
15 the aforesaid materials may also be employed.

The term "polyester polyol" as used in this specification and claims includes any minor amounts of unreacted polyol remaining after the preparation of the polyester polyol and/or unesterified polyol (for example, glycol) added after the preparation of the polyester  
20 polyol. Suitable polyester polyols can be produced, for example, from organic dicarboxylic acids with 2 to 12 carbons, preferably aliphatic dicarboxylic acids with 4 to 6 carbons, and multivalent alcohols, preferably diols, with 2 to 12 carbons, preferably 2 to 6 carbons. Examples of dicarboxylic acids include succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic  
25 acid, isophthalic acid, and terephthalic acid. The dicarboxylic acids can be used individually or in mixtures. Instead of the free dicarboxylic acids, the corresponding dicarboxylic acid derivatives may also be used such as dicarboxylic acid mono- or di- esters of alcohols with 1 to 4 carbons, or dicarboxylic acid anhydrides. Dicarboxylic acid mixtures of succinic acid, glutaric acid and adipic acid in quantity ratios of 20:35:35- 50:20- 32 parts by weight are  
30 preferred, especially adipic acid. Examples of divalent and multivalent alcohols, especially diols, include ethanediol, diethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, 1,4- butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerine and trimethylolpropanes, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol,

tetramethylene glycol, 1,4-cyclohexane- dimethanol, ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6- hexanediol, or mixtures of at least two of these diols are preferred, especially mixtures of 1,4-butanediol, 1,5-pentanediol, and 1,6- hexanediol.

Furthermore, polyester polyols of lactones, for example, epsilon- caprolactone or

5 hydroxycarboxylic acids, for example, omega- hydroxycaproic acid, may also be used.

While the aromatic polyester polyols can be prepared from substantially pure reactant materials, more complex ingredients are advantageously used, such as the side stream, waste or scrap residues from the manufacture of phthalic acid, terephthalic acid, dimethyl terephthalate, and polyethylene terephthalate. Other residues are dimethyl terephthalate

10 (DMT) process residues, which are waste or scrap residues from the manufacture of DMT.

The present applicants have observed that for certain applications it is particularly advantageous for reasons of foam performance and processing to have present in the polyol composition both the "Novolak" polyol and an additional aromatic polyol which can be an aromatic polyether or aromatic polyester polyol.

15

Polyether polyols that additionally may be present include those which can be obtained by known methods. For example, polyether polyols can be produced by anionic polymerization with alkali hydroxides such as sodium hydroxide or potassium hydroxide or alkali alcoholates, such as sodium methylate, sodium ethylate, or potassium ethylate or potassium isopropylate as catalysts and with the addition of at least one initiator molecule containing 2 to 8, preferably 3 to 8, reactive hydrogens or by cationic polymerization with Lewis acids such as antimony pentachloride, boron trifluoride etherate, etc., or bleaching earth as catalysts from one or more alkylene oxides with 2 to 4 carbons in the alkylene radical. Any suitable alkylene oxide may be used such as 1,3-propylene oxide, 1,2- and 2,3- butylene oxide, amylene oxides, styrene oxide, and preferably ethylene oxide and 1,2- propylene oxide and mixtures of these oxides. The polyalkylene polyether polyols may be prepared from other starting materials such as tetrahydrofuran and alkylene oxide- tetrahydrofuran mixtures; epihalohydrins such as epichlorohydrin; as well as aralkylene oxides such as styrene oxide. The polyalkylene polyether polyols may have either primary or secondary hydroxyl groups, preferably secondary hydroxyl groups from the addition of propylene oxide onto an initiator because these groups are slower to react. Included among the polyether polyols are polyoxyethylene glycol, polyoxypropylene glycol, polyoxybutylene glycol, polytetramethylene glycol, block copolymers, for example,

30



combinations of polyoxypropylene and polyoxyethylene glycols, poly-1,2-oxybutylene and polyoxyethylene glycols, poly-1,4-tetramethylene and polyoxyethylene glycols, and copolymer glycols prepared from blends or sequential addition of two or more alkylene oxides. The polyalkylene polyether polyols may be prepared by any known process such as, for example, the process disclosed by Wurtz in 1859 and Encyclopedia of Chemical Technology, Vol. 7, pp. 257- 262, published by Interscience Publishers, Inc. (1951) or in U.S. Pat. No. 1,922,459. Polyethers which are preferred include the alkylene oxide addition products of polyhydric alcohols such as ethylene glycol, propylene glycol, dipropylene glycol, trimethylene glycol, 1,2- butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, hydroquinone, resorcinol glycerol, glycerine, 1,1,1-trimethylol- propane, 1,1,1-trimethylolethane, pentaerythritol, 1,2,6-hexanetriol, a- methyl glucoside, sucrose, and sorbitol. Also included within the term "polyhydric alcohol" are compounds derived from phenol such as 2,2- bis(4- hydroxyphenyl)-propane, commonly known as Bisphenol A. Particularly preferred in the polyol composition is at least one polyol which is initiated with a compound having at least two primary or secondary amine groups, a polyhydric alcohol having 4 or more hydroxyl groups, such as sucrose, or a mixture of initiators employing a polyhydric alcohol having at least 4 hydroxyl groups and compounds having at least two primary or secondary amine groups. Suitable organic amine initiators which may be condensed with alkylene oxides include aromatic amines such as aniline, N-alkylphenylene-diamines, 2,4'-, 2,2'-, and 4,4'-methylenedianiline, 2,6- or 2,4-toluenediamine, vicinal toluenediamines, o-chloro-aniline, p- aminoaniline, 1,5-diaminonaphthalene, methylene dianiline, the various condensation products of aniline and formaldehyde, and the isomeric diaminotoluenes; and aliphatic amines such as mono-, di-, and trialkanolamines, ethylene diamine, propylene diamine, diethylenetriamine, methylamine, triisopropanolamine, 1,3- diaminopropane, 1,3-diaminobutane, and 1,4-diaminobutane. Preferable amines include monoethanolamine, vicinal toluenediamines, ethylenediamines, and propylenediamine. Yet another class of aromatic polyether polyols contemplated for use in this invention are the Mannich-based polyol an alkylene oxide adduct of phenol/formaldehyde/alkanolamine resin, frequently called a "Mannich" polyol such as disclosed in U.S. Patents 4,883,826; 4,939,182; and 5,120,815.

When the blowing agent composition includes physical blowing agents such as, for example, HFC245fa, HFC134a , HFC365mfc or HFC227, or hydrocarbons such as for

example n-pentane, the combination of an aromatic polyester polyol and an aromatic polyether polyols is particularly preferred in order to achieve desirable flame retardant and smoke suppressant characteristics together with attractive storage stability of the polyol composition and convenient foam processing.

5

In the practice of the present invention, the applicants have observed that for the purpose of enhancing foam integrity and improving surface adhesion it is advantageous to incorporate small amounts of high equivalent weight polyether polyols such as are typically used in molded flexible polyurethanes, for example, VORANOL 1421 available from The Dow Chemical Company and understood to be a glycerine-initiated polyoxypropylene-oxyethylene polyol having a molecular weight of approximately 5100 and an oxyethylene content of approximately 70 percent.

In addition to the foregoing components, it is often desirable to have certain other ingredients present in the polyol composition for the purpose of facilitating the subsequent use in preparing cellular polymers. Among these additional ingredients are catalysts, surfactants, preservatives, colorants, antioxidants, flame retardants, reinforcing agents, stabilizers and fillers. In making polyurethane foam, it is generally highly preferred to employ a minor amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants advantageously comprise a liquid or solid organosilicone surfactant. Other, less preferred surfactants include polyethylene glycol ethers of long-chain alcohols, tertiary amine or alkanolamine salts of long-chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the formation of large, uneven cells. Typically, 0.2 to 3 parts of the surfactant per 100 parts by weight polyol composition are sufficient for this purpose.

Such flame retardants advantageously present include for example exfoliating graphite, phosphonate esters, phosphate esters, halogenated phosphate esters or a combination thereof. Phosphonate esters for use in the present invention can be represented by the formula  $R-P(O)(OR')(OR'')$  where R, R' and R'' are each independently an alkyl having 1 to 4 carbon atoms. Preferred members of this group are dimethyl methylphosphonate (DMMP) and diethyl ethyl phosphonate (DEEP). Phosphate esters

which can be used in the present invention are trialkyl phosphates, such as triethyl phosphate, and tricresyl phosphate. When used, the phosphonate or phosphate ester flame retardants are present in the final foam at a level of from 0.5 to 20 percent by weight of the final foam. Preferably they are 1 to 15 percent by weight of the final foam. More preferably they constitute 2 to 10 percent by weight of the final foam. Halogenated phosphate esters which are associated with fire retardation are known in the art and can be represented by the general formula  $P(O)(OR'X'n)(OR''X''n)(OR'''X'''n)$ , where R', R'' and R''' are each independently an alkyl having 1 to 4 carbon atoms, X', X'' and X''' are each independently a halogen and n is an integer from 1 to 3. Examples of halogenated phosphate esters include 2-chloroethanol phosphate; 1-chloro-2-propanol phosphate [tris(1-chloro-2-propyl) phosphate] (TCPP); 1,3-dichloro-2-propanol phosphate also called tris(1,3-dichloro-2-propyl) phosphate; tri(2-chloroethyl) phosphate; tri(2,2-dichloroisopropyl) phosphate; tri(2,3-dibromopropyl) phosphate; tri(1,3-dichloropropyl)phosphate; tetrakis(2-chloroethyl) ethylene diphosphate; bis(2-chloroethyl) 2-chloroethylphosphonate; clphosphates [2-chloroethyl diphosphate]; tetrakis(2-chloroethyl) ethylenediphosphate; tris-(2-chloroethyl)-phosphate, tris-(2-chloropropyl)phosphate, tris-(2,3-dibromopropyl)-phosphate, tris(1,3-dichloropropyl)phosphate tetrakis(2-chloroethyl-ethylene diphosphate and tetrakis(2-chloroethyl) ethyleneoxyethylenediphosphate. Tribromonopentyl chloroalkyl phosphates as disclosed in EP 0 735 039 having the formula

$[(BrCH_2)_3C-CH_2O]_n PO (OCYHCH_2Cl)_3$  -where Y represents a hydrogen, an alkyl having 1 to 3 carbon atoms, or chloroalkyl group and n is from 0.95 to 1.15 may also be used.

One or more catalysts for the reaction of the polyol (and water, if present) with the polyisocyanate are advantageously used. Any suitable urethane catalyst may be used, including tertiary amine compounds and organometallic compounds. Exemplary tertiary amine compounds include triethylenediamine, N-methylmorpholine, N,N-dimethylcyclohexylamine, pentamethyldiethylenetriamine, tetramethylethylenediamine, 1-methyl-4-dimethylaminoethylpiperazine, 3-methoxy-N-dimethylpropylamine, N-ethylmorpholine, diethylethanolamine, N-cocomorpholine, N,N-dimethyl-N',N'-dimethyl isopropylpropylenediamine, N,N-diethyl-3-diethylaminopropylamine and dimethylbenzylamine. Exemplary organometallic catalysts include organomercury, organolead, organoferric and organotin catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids

such as dibutyltin di-laurate, as well as other organometallic compounds such as are disclosed in U.S. Patent 2,846,408. A catalyst for the trimerization of polyisocyanates, resulting in a polyisocyanurate, such as an alkali metal alkoxide may also optionally be employed herein. Such catalysts are used in an amount which measurably increases the rate of polyurethane or polyisocyanurate formation. Typical amounts are 0.001 to 3 parts of catalyst per 100 parts by weight of total polyol.

A polyisocyanate-based foam is obtained by bringing together the above described polyol composition under foaming forming conditions with a polyisocyanate. In this manner polyurethane or polyisocyanurate foam can be prepared. Polyisocyanates useful in making the foam include aliphatic and cycloaliphatic and preferably aromatic polyisocyanates or combinations thereof, advantageously having an average of from 2 to 3.5, preferably from 2.4 to 3.2, and more preferably from 2.8 to 3.2 isocyanate groups per molecule. A crude polyisocyanate may also be used in the practice of this invention, such as crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamine or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude methylene diphenylamine. The preferred polyisocyanates are aromatic polyisocyanates such as disclosed in U.S. Patent 3,215,652. Especially preferred are methylene-bridged polyphenyl polyisocyanates and mixtures thereof with crude diphenylmethane diisocyanate, due to their ability to cross-link the polyurethane.

For the preparation of a polyurethane foam the polyisocyanate is present in an amount, relative to the polyol composition, so as to provide an isocyanate reaction index of from 80 to 150, preferably from 90 to 130. An isocyanate index of 100 corresponds to one isocyanate equivalent per active hydrogen atom present in the polyol composition. For the preparation of a polyisocyanurate foam the polyisocyanate is present in an amount to provide an isocyanate reaction index of from 150 to 600, preferably from 200 to 500. The polyol composition of this invention is particularly useful in the preparation of polyisocyanurate foam.

In general, the rigid foams may be produced by discontinuous or continuous processes, including the process referred to generally as the discontinuous panel process (DCP) and continuous lamination, with the foaming reaction and subsequent curing being

carried out in molds or on conveyors. When utilizing the foams in laminates, the facing may be flexible, for example, aluminum foil or coated paper, or may be a rigid material such as plaster-board, polyester facing or steel facing. Other processes to prepare construction foams are known as spray and block foams.

5

The rigid foam of the present invention are for the most part closed-cell foam. By closed-cells it is meant that at least 75 percent, preferably 80 percent or greater, and more preferably 85 percent or more of the cells are closed. In a preferred embodiment, 90 percent or more of the cells are closed. Because of the closed-cell structures, the rigid polyurethanes of the present invention are useful for thermal insulation applications such as roofing, sheathing and in-situ spray applications.

10

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are by weight. The following abbreviations identify various materials used in the Examples.

15

Polyol A: A "Novolak" polyol being a oxypropylene-oxyalkylene adduct based on a phenol-formaldehyde condensate having an average functionality of about 3.3. Polyol hydroxyl number is 196.

20

Polyol B A polyester polyol, TEROL 198 available from Oxid understood to have a hydroxyl number 198 .

Polyol C A glycerine-initiated oxypropylene-oxyethylene polyol, VORANOL 1421, available from The Dow Chemical Company. Hydroxyl Number 35.

25

Polyol D A sucrose initiated oxypropylene-oxyethylene polyol, VORANOL 280, available from The Dow Chemical Company. Hydroxyl Number 280

30	DEEP	Diethyl ethylphosphonate
	TCPP	Trichloroisopropylphosphate
	MEG	ethylene glycol
	DABCO DC5598	Surfactant, available from Air Products
	DABCO TMR	Catalyst, available from Air Products

	DABCO K15	Catalyst, available from Air Products
	PMDETA	pentamethyldiethylenetriamine
	DMCHA	dimethylcyclohexylamine
	Toyocat DM70	Catalyst ,available from Tosoh
5	Curithane 206	Catalyst available from The Dow Chemical Company
	Formic Acid	Purity 98 percent , supplied by Incofar
	n-pentane	commercial grade as provided by Synthesis
	ISO A	VORANATE 600, A higher functionality (2.9 to 3) crude diphenylmethane diisocyanate available from The Dow Chemical 10 Company
	ISO B	VORANATE 220, A standard grade crude diphenylmethane diisocyanate available from The Dow Chemical Company

#### Foam Examples 1-9

15           Foams 1 to 9 (2, 4 , 7 and 9 are comparative Foams) are prepared using a Cannon  
A40 high pressure machine. Reactants and amounts are indicated in the following table.  
Foams 1 – 4 have been evaluated in the production of metal-faced continuous laminate  
panels. Foams 5 to 9 have been evaluated in the production of discontinuous panels.  
Foams prepared in the presence of formic acid exhibit a notably stronger flame retardant  
20 and smoke suppressant characteristics than those foams prepared in the absence of the acid.  
Foams prepared in the presence of formic acid and pentane, provided both surprisingly good  
flame retardant and reduced smoke generation traits; such performance in the presence of  
pentane had not been expected giving consideration to the normal flammable properties of  
pentane.

25           Comparative example Foam 9 show that use of a polyol composition comprising  
uniquely an aromatic polyester polyol is unattractive with observation of poor skin curing,  
resulting in more difficult processing.

30           A further observation is that this invention provides for polyol compositions of  
attractive storage stability where such compositions includes as blowing agent, HFC245fa  
(Foam 8).

Foam Example 10

A polyisocyanurate foam is prepared in a manner similar to Foams 1-9 with reactants as noted below. In this instance the polyol composition is a combination of an aromatic polyester polyol and an aromatic polyether polyol with good blend stability in the presence of the blowing agent, pentafluoropropane (245fa).

47 pbw	TERATE 4026 , a polyester polyol from Kosa, OH value 205
7	Polyol C
10	TERACOL 5902, a TDA initiated, oxypropylene - oxyethylene polyol
10	available from The Dow Chemical Company, OH value 375
5	DEEP
9	TCPP
6	TEP surfactant
1.6	Surfactant
15	0.3 DMCHA
	2.2 CURITHANE 206
	0.3 water
	2.6 formic acid
	9.1 Hfc 245fa

Iso A (Index) 170 pbw /(300)

Reactivity (CT/GT) 4/44

Free rise density (kg/m3) 38.3

The foam is observed to have a Butler chimney flame spread of 15.5 cm; a weight retention of 93.4 percent; and a smoke development (NBS) of 59. Processing characteristics of the foam are attractive with a 100 percent skin cure being noted in about 7 minutes at a mold temperature of 45C.

Table 1

Pbw	Foam 1	Foam 2*	Foam 3	Foam 4*	Foam 5	Foam 6	Foam 7*	Foam 8	Foam 9*
Polyol A	30.1	30	31	31	52.3	45.4	51	24.8	
Polyol B	25	25	30.5	30.5	/	/	/	24.7	47.6 (*)
Polyol C	11.5	11.5	/	/	/	/	/		
Polyol D	/	/	9.1	9.1	/	/	/		
DEEP	11.5	11.4	9.8	9.8	8	12.9	11	8	12.89
TCP	14	14	9.8	9.8	30	31.7	31.9	30	30.25
MEG	/	/	0.5	0.5	/	/	/		
L6900	/	/	/	/	/	1.98	1.5		
DABCO DC5598	1.8	1.8	2.95	2.95	3	/	/	3	3
DMCHA	0.47	0.4			0.2	/	/	0.05	
DMEE	/	/	/	/	/	0.2	/		
Toyocat DM70	0.2								
PMDETA	/	0.07	0.1	0.1	/	/	/		
CURITHANE 52	/	/	4.92	4.92	/	3.03	/		
Dabco K15	0.33								
CURITHANE 206	1.74	2.2	/	/	1.5	/	0.7	1.45	1.5
DABCO TMR	/	/	1.0	1.0	/	/	/		
Water	1.91	3.15	/	1.2	/	1.98	3.12		1.98
Formic Acid	1.45	/	1.6	/	4.99	2.78	/	4	2.78
HFC 245fa	/	/	/	/	/	/	/	4	/
n-Pentane	/	/	9	9	/	/	/	/	/
ISO A (Index)	188.5 (300)	231 (300)	180 (340)	180 (320)	/	/			
ISO B	/	/	/	/	160 (293)	168 (240)	180 (247)	143 (290)	179 (240)
Polyol blend stability	Clear ,stable	Clear ,stable	/		Clear ,stable	Clear ,stable	Clear ,stable	Clear ,stable	
Reactivity CT/GT (secs)	5 / 42	5 / 26	6 / 41		6 / 95	12 / 100	13 / 88	6/83	20/105
Free-Rise Core density (kg/m <sup>3</sup> )	44.9	43.3	38.9		34	31	35	32.4	35
DIN 4102 B2 rating (cm)	5	/	6.5	9.2	6	9	12.5	6.4	7.8
Butler Chimney test									
Flame spread	15.9	20 cm	/						
Weight retention	cm 92.6 percent	91.5	89.8	87					
Smoke development (NBS)									
	137	176	66	86					
% skin cure (45-50C mold temp)	>70 percent at 7min	25 percent at 7 min	100 percent at 5 min	25 percent at 5 min	100 percent 12 min	100 percent 12 min	70 percent (soft foam) 12'	100 percent 12 min	50 percent (soft foam) 12'

(\*) Terate 2540, polyester polyol from Kosa, hydroxyl number 250



Examples 11-15:Effect of formic acid on flammability characteristics of polyisocyanurate foams.

5 Foams 11 to 15 are prepared under hand mix conditions in accordance with the reactants and amounts indicated in the Table 2. The combustion characteristics of the foams as monitored by cone calorimetry indicate that use of formic acid in a select range provides a robust performance despite a variance in isocyanate reaction.

10

Table 2

Pbw	Foam 11	Foam 12	Foam 13	Foam 14	Foam 15
TERATE 4026	45	45	45	45	45
Polyol C	7	7	7	7	7
TERACOL 5902	10	10	10	10	10
EMPILAN NP 9	2	2	2	2	2
DEEP	5	5	5	5	5
TCPP	9	9	9	9	9
TEP	6	6	6	6	6
DABCO DC5598	1.5	1.5	1.5	1.5	1.5
Water	0.2	0.2	0.2	0.2	0.2
DMCHA	0.3	0.3	0.3	0.3	0.3
CURITHANE 52	1.8	2.1	1.2	3	1.2
Formic Acid	3	2.1	1.2	3	1.2
HFC 245fa	8	11	14.5	7	17
ISO A to give Reaction Index of:	300	287	380	294	385
Theoretical trimer percent	43.4	41.5	49.9	43.3	50.4
Reactivity CT/GT/TFT (secs) @ 20°C	8 75 145	8 55 124	9 70 150	8 60 135	8 58 110
Free-Rise Core density (kg/m <sup>3</sup> )	36.3	35.5	37.6	35.8	35.6
Cone Calorimeter Peak Heat Release (kW/m <sup>2</sup> )	96	102	84.5	77.5	113
Cone Calorimeter mass loss %	39.5	40.5	41.5	41	43

## Foam Examples 16-19

Flammability characteristics of formic acid modified polyisocyanurate foams with various physical blowing agents.

5        Foams 16 to 19, typical of a discontinuous panel system, are prepared using a Cannon A40 high pressure machine. Reactants and amounts are indicated in Table 3.

      The results indicate the ability to use formic acid in combination with other blowing agents when preparing polyisocyanurate foams that exhibit good flame retardant  
10 characteristics.

      All foaming systems were observed as having easy processing characteristics good attractive physical properties including adhesion to metal facers. Use of the formic acid as sole blowing agent while still providing for good FR properties is observed to give foams  
15 with poorer physical properties than these reported here. It is also desirable to utilize water in restricted amounts within the system; use of significantly elevated amounts of water leads to foam systems that are more arduous to process and foams that may be friable and inferior in their FR performance

Table 3

Pbw	Foam 16	Foam 17	Foam 18	Foam 19
TERATE 4026	45	45	45	45
Polyol C	7	7	7	7
TERACOL 5902	10	10	10	10
SURFACTANT	2	2	2	2
DEEP	5	5	5	5
TCPP	9	9	9	9
TEP	6	6	6	6
DABCO DC5598	1.5	1.5	1.5	1.5
Water	0.2	0.3	0.2	0.2
DMCHA	0.3	0.3	0.3	0.3
CURITHANE 52	2.2	2.2	2.2	2.2
Formic Acid	2.6	2.6	2.6	2.6
HCFC 141B	12			
HFC 245fa		12		
n-Pentane				6
HFC365 / 227 (93;7 wt ratio)			12	
ISO A to give Reaction Index of:	310	310	310	290
Reactivity CT/GT/ (secs) @ 20°C	6 34	4 32	5 41	4 38
Free-Rise Core density (kg/m <sup>3</sup> )	35.5	35.3	40.3	35.4
Cone Calorimeter Peak Heat Release (kW/m <sup>2</sup> )	94	88.5	99	103
Cone Calorimeter mass loss after 500s ( percent)	39.5	43.0	41.0	40.0
LOI (ASTM 2863)	29.5	28.5	29	/
DIN 4102 B2 (cm)	5.2	5.7	5.5	6

Other embodiments of the invention will be apparent to those skilled in the art from  
5 a consideration of this specification or practice of the invention disclosed herein. It is  
intended that the specification and examples be considered as exemplary only with the true  
scope and spirit of the invention being indicated by the following claims.

## CLAIMS:

- 1) A polyol composition suitable for the preparation of a rigid polyisocyanate-based foam containing one or more polyether or polyester polyols and a blowing agent, wherein;
  - 5 a) the blowing agent comprises formic acid; and
  - b) the polyol comprises an aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of a phenol with an aldehyde.
- 2) The polyol composition of Claim 1 which additionally comprises a physical blowing agent.
- 10 3) The polyol composition of Claim 2 wherein the physical blowing agent is a hydrocarbon selected from the group consisting of butane, pentane, cyclopentane, hexane, cyclohexane, and heptane, and the isomers thereof.
- 4) The polyol composition of Claim 2 wherein the physical blowing agent is a C<sub>1</sub>-C<sub>4</sub> hydrofluoroalkane or hydrochlorofluoroalkane.
- 15 5) The polyol composition of Claim 4 wherein the physical blowing agent is a hydrofluoroalkane selected from the group consisting of difluoromethane, difluoroethane, tetrafluoroethane, pentafluoropropane and hexafluorobutane.
- 6) The polyol composition of Claim 1 where in the aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of phenol with formaldehyde.
- 20 7) The polyol composition of Claim 6 wherein the aromatic polyoxyalkylene polyol is present in an amount of at least 20 weight percent based on total weight of the polyol composition.
- 8) The polyol composition of Claim 7 that further comprises an aromatic polyester polyol.
- 9) A multi component system suitable for the preparation of rigid polyisocyanate-based foam that comprises as first component an aromatic polyisocyanate, and as second  
25 component a polyol composition as claimed in Claim 1.

- 10) A process for preparing a polyisocyanate-based foam which comprises bringing together under foam-forming conditions a polyisocyanate with a polyol composition as claimed in Claim 1.
- 11) The process of Claim 10 where in the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 80 to 150.
- 12) The process of Claim 10 where in the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 150 to 600.
- 13) A polyurethane foam obtained by bringing together under foam-forming conditions a polyisocyanate with a polyol composition characterized in that:
- a) the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 80 to 150; and
- b) the polyol composition comprises (i) formic acid; and (ii) an aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of a phenol with an aldehyde.
- 14) A polyisocyanurate foam obtained by bringing together under foam-forming conditions a polyisocyanate with a polyol composition characterized in that:
- a) the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from 150 to 600; and
- b) the polyol composition comprises (i) formic acid; and (ii) an aromatic polyoxyalkylene polyol based on an initiator obtained from the condensation of a phenol with an aldehyde.
- 15) A laminate comprising the foam of Claim 13 or Claim 14.
- 16) A process for preparing a closed-celled polyisocyanurate foam by bringing into contact under foam-forming conditions a polyisocyanate with a polyol composition in the presence of a blowing agent mixture wherein the polyol composition comprises an aromatic polyester polyol and an aromatic polyether polyol; and wherein the blowing agent mixture comprises formic acid and a hydrofluoroalkane selected from the group

consisting of tetrafluoroethane, pentafluoropropane, heptafluoropropane and pentafluorobutane, and characterized in that the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from greater than 150 to 600.

17) The process of Claim 16 wherein water is present in an amount of from 0 to 2 parts by weight per 100 parts of the combined weight of the polyol composition and blowing agent mixture.

18) The process of Claim 16 wherein the aromatic polyether polyol comprises a toluenediamine-initiated polyol, a Mannich base-initiated polyol, a methylene diphenylamine-initiated polyol, a phenol-acetone condensate-initiated polyol or a phenol-formaldehyde condensate-initiated polyol.

19) A process for preparing a closed-celled polyisocyanurate foam by bringing into contact under foam-forming conditions a polyisocyanate with a polyol composition in the presence of a blowing agent mixture wherein the polyol composition comprises an aromatic polyester polyol and an aromatic polyether polyol; and wherein the blowing agent mixture comprises formic acid and a hydrocarbon selected from the group consisting of butane, pentane, cyclopentane, hexane, cyclohexane, and heptane, and the isomers thereof and characterized in that the polyisocyanate is present in an amount to provide for an isocyanate reaction index of from greater than 150 to 600.

20) The process of Claim 16 or 19, wherein the polyisocyanate is an aromatic polyisocyanate having on average from 2.8 to 3.2 isocyanate groups per molecule.

21) A two component foam forming system that comprises:

a) an aromatic polyisocyanates having an average of from 2.8 to 3.2 isocyanate groups per molecule; and

b) a polyol composition that contains (i) an aromatic polyester polyol and an aromatic polyether polyol; and (ii) a blowing agent mixture which comprises formic acid and a hydrofluoroalkane selected from the group consisting of tetrafluoroethane, pentafluoropropane, heptafluoropropane and pentafluorobutane.

22) A two component foam forming system that comprises:

a) an aromatic polyisocyanates having an average of from 2.8 to 3.2 isocyanate groups per molecule; and

b) a polyol composition that contains: (i) an aromatic polyester polyol and an aromatic polyether polyol; and (ii) a blowing agent mixture which comprises formic acid and a hydrocarbon selected from the group consisting of butane, pentane, cyclopentane, hexane, cyclohexane, and heptane, and the isomers thereof.

# INTERNATIONAL SEARCH REPORT

International Application No.  
P US 03/41607

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G18/54 C08J9/08 C08J9/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 483 431 A (MITSUI TOATSU CHEMICALS) 6 May 1992 (1992-05-06) page 3, line 46 - page 4, line 49 page 8, line 10 - page 8, line 16 table 1 tables 19-22 claims 1-4,30,37	1-22
A	US 4 046 721 A (AUSTIN THOMAS H ET AL) 6 September 1977 (1977-09-06) column 2, line 17 - column 3, line 6 column 4, line 22 - column 4, line 31 table I claims 1-3,7,8	1-22
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

In International Application No.

PCT/US 2003/41607

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No

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